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The Physics and the Chemistry of ETWAC Code (An Early Time Wet Air Chemistry Code for Disturbed Air Conductivity Calculations)

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The physics and the chemistry of dry and wet air disturbed by an electron beam, is described. The pertinent reactions controlling the deionization and hence the air conductivity is presented.

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THE PHYSICS AND THE CHEMISTRY OF ETWAC CODE (AN EARLY TIME WET AIR CHEMISTRY CODE FOR DISTURBED AIR CONDUCTIVITY CALCULATIONS)

I. INTRODUCTION

When air is bombarded by a pulsed beam of electrons or charged particles, a conducting ionized path is generated which will subsequently decay and deionize. The conductivity of the plasma is determined by the electron density in the ionized region. However, the electron density or the deionization of the plasma depends on the atmospheric ions generated as a result of the energy deposited in air by the bombarding charged particles.

The air ions, their forms and their paths in the deionization scheme depend on the air density, various kinetic temperatures and the density of the minor species present in air. Minor species and impurities (H_2O, O_3, CO_2, NO, NO_2, N_2O, etc.) are generally present in the atmosphere. Their role in the deionization of air must be assessed.

In this report we present the physics and the chemistry of a code developed to depict the role of the water vapor in the deionization of air. This code is developed to provide calculations on the time history of the electron density, at a point in space, during the passage of an electron beam in wet air. The code is named ETWAC (Early Time Wet Air Chemistry) to emphasize its application to the early time phase of the disturbed air.

The report describes the deionization of the dry air in Section 2. In Section 3 the processes which arise upon the addition of water vapor to air are presented to depict the role of H_2O in the deionization processes. In Section 4 the rate coefficients currently used in

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the code are presented while in Section 5 a discussion is given for the calculation of various relevant temperatures.

II. THE CHEMISTRY OF DRY AIR

The ionization of the air species (N_2 and O_2) by the electron beam arise from the collisional ionization, ionization due to the Bremsstrahlung radiation and the avalanche ionization caused by the intense electric field associated with the electron beam. Regardless of the ionization sources, the following ions: N_2^+, N^+, O_2^+, and O^+, are generated directly in the dry air along with the free electrons.

The deionization (i.e. the disappearance of the charges, positive and negative) proceeds in two distinct manners: 1) by the electron-ion recombinations and 2) by the ion-ion recombinations. These processes[1], however, are complimented by various atomic processes which result in the generation of other ions not produced originally in air.

The electron-ion recombinations proceed through the dissociative and the three-body recombinations. The dissociative recombinations are:

$$e + N_2^+ \rightarrow N + N \tag{1}$$

$$e + N_3^+ \rightarrow N + N_2 \tag{2}$$

$$e + N_4^+ \rightarrow N_2 + N_2 \tag{3}$$

$$e + O_2^+ \rightarrow O + O \tag{4}$$

$$e + O_4^+ \rightarrow O_2 + O_2 \tag{5}$$

$$e + NO^+ \rightarrow N + O \tag{6}$$

$$e + O_2^+ \cdot N_2 \rightarrow O_2 + N_2 \tag{7}$$

The three-body recombinations, on the other hand, proceed according to

$$e + e + A_n^+ \rightarrow e + A_n \tag{8}$$

and

$$e + M + A_n^+ \rightarrow M + A_n \tag{9}$$

Where the third-body, M, in equation (9) is a neutral species and A_n^+ indicates an atomic ion (n=1), a molecular ion (n=2) or a cluster ion (n=3 and 4). Recombination also proceeds through the radiative recombination, which can be ignored in regions of interest to our problem.

The cluster ions, N_3^+ , N_4^+, O_4^+ and $O_2^+ \cdot N_2$ which appear in equations (2), (3), (5) and (7) are formed by the following association reactions

$$N^+ + N_2 + N_2 \rightarrow N_3^+ + N_2 \tag{10}$$

$$N_2^+ + N_2 + N_2 \rightarrow N_4^+ + N_2 \tag{11}$$

$$O_2^+ + O_2 + O_2 \rightarrow O_4^+ + O_2 \tag{12}$$

$$O_2^+ + N_2 + N_2 \rightarrow O_2^+ . N_2 + N_2 \tag{13}$$

NO^+ on the other hand, is formed by

$$O^+ + N_2 \rightarrow NO^+ + N \tag{14}$$

$$N^+ + O_2 \rightarrow NO^+ + O \tag{15}$$

and by various charge exchange processes of positive ions with NO. However, for early time phase of the beam air interaction one may

ignore NO^+.

The ion-ion recombination, also called the mutual neutralization can be illustrated by the following two reactions

$$O_2^- + A_n^+ \rightarrow O_2 + A_n \tag{16}$$

$$O^- + A_n^+ \rightarrow O + A_n \tag{17}$$

Mutual neutralization also proceeds through the three-body neutralization reaction

$$(O^-, O_2^-) + A_n^+ + M \rightarrow (O, O_2) + A_n + M \tag{18}$$

where the negative ions O_2^- and O^- are produced by the three-body

$$e + O_2 + O_2 \rightarrow O_2^- + O_2 \tag{19}$$

$$e + O_2 + N_2 \rightarrow O_2^- + N_2 \tag{20}$$

and by the dissociative attachments

$$e + O_2 \rightarrow O^- + O \quad , \tag{21}$$

respectively.

The positive ions, however, undergo various charge exchange and ion atom interchange processes which are

$$N_2^+ + O_2 \rightarrow O_2^+ + N_2 \tag{22}$$

$$N^+ + O_2 \rightarrow O_2^+ + N \tag{23}$$

$$O^+ + O_2 \rightarrow O_2^+ + O \tag{24}$$

$$N_4^+ + O_2 \rightarrow O_2^+ + 2N_2 \tag{25}$$

$$N_3^+ + O_2 \rightarrow NO^+ + N_2 \tag{26}$$

$$N_3^+ + O_2 \rightarrow NO^+ + N_2O \tag{27}$$

$$O_2^+ \cdot N_2 + O_2 \rightarrow O_4^+ + N_2 \tag{28}$$

A schematic diagram shown in Fig. 1 illustrates the flow of the positive charge in the deionization scheme of the disturbed dry air.

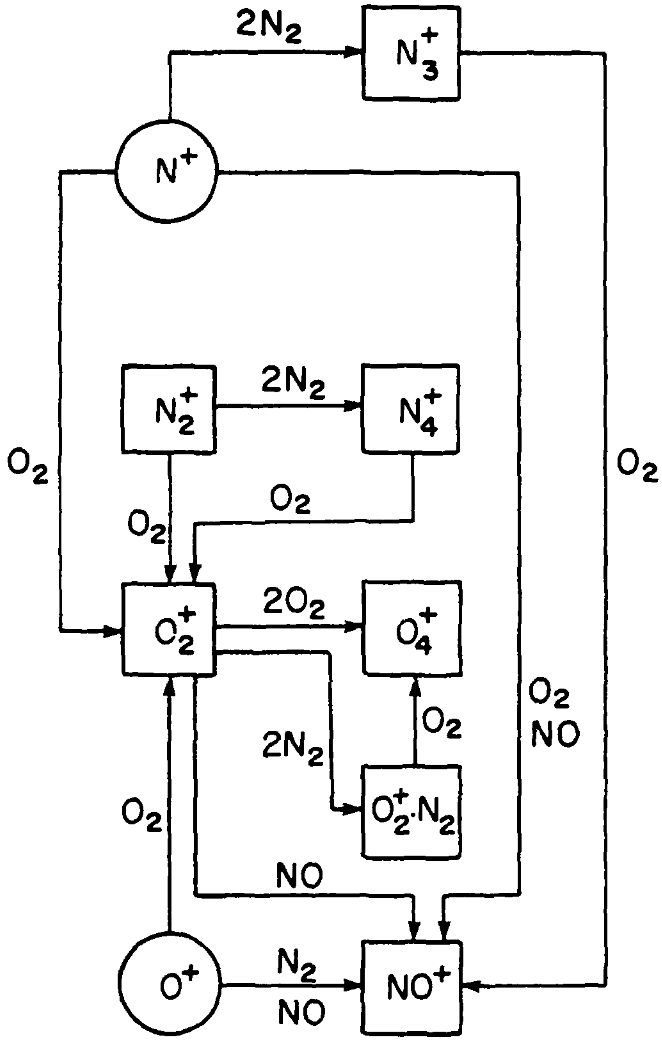

Fig. 1 — Disturbed dry air positive ion flow chart

III. THE CHEMISTRY OF WET AIR

The presence of water in air introduces further complications in the disturbed air chemistry. Various positive clustered ions are formed which terminate in the form of a hydrated hydronium, $H_3O^+ \cdot (H_2O)_n$. These ions have been observed by Narcisi and Bailey[2] in the D-region of the ionosphere. The reaction paths leading towards these clusters starts with O_2^+ as a precursor ion and is well understood[3,4] and have been utilized in the modeling[1,5] of the disturbed atmosphere as a result of nuclear detonation.

The hydrated hydronium generally recombine with the free electrons, through the dissociative recombination, at a much faster[6] rate compared to the lighter air ions.

The pertinent reactions which lead to the generation of various hydrated ions are as follows. The positive ions, N^+, N_2^+, N_3^+, N_4^+ and O^+ react with H_2O according to the following reactions

$$N^+ + H_2O \rightarrow H_2O^+ + N \tag{29}$$

$$N_2^+ + H_2O \rightarrow H_2O^+ + N_2 \tag{30}$$

$$N_2^+ + H_2O \rightarrow N_2H^+ + OH \tag{31}$$

$$N_2^+ + H_2O \rightarrow H_2NO^+ + N_2 \tag{32}$$

$$N_4^+ + H_2O \rightarrow H_2O^+ + 2N_2 \tag{33}$$

$$O^+ + H_2O \rightarrow H_2O^+ + O \tag{34}$$

Reactions (29) through (34) obviously produce predominantly H_2O^+ which in turn undergoes the following reactions

$$H_2O^+ + O_2 \rightarrow O_2^+ + H_2O \tag{35}$$

$$H_2O^+ + e \rightarrow OH + H \qquad (36)$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \qquad (37)$$

Reaction (37) generates the hydronium, H_3O^+, which in turn generates once hydrated hydronium according to

$$H_3O^+ + H_2O + M \rightarrow H_3O^+ \cdot H_2O + M \qquad (38)$$

The following reactions, an association and two switching, result in the production of $O_2^+ \cdot H_2O$

$$O_2^+ + H_2O + M \rightarrow O_2^+ \cdot H_2O + M \qquad (39)$$

$$O_4^+ + H_2O \rightarrow O_2^+ . H_2O + M \qquad (40)$$

$$O_2^+ \cdot N_2 + H_2O \rightarrow O_2^+ \cdot H_2O + N_2 \qquad (41)$$

On the other hand, $O_2^+ \cdot H_2O$ reacts with H_2O to produce $H_3O^+ \cdot OH$ which in turn produces $H_3O^+ \cdot H_2O$ through a switching reaction with H_2O. This indicates two routes for the production of $H_3O^+ \cdot H_2O$, one initiated by H_3O^+, and the other by $O_2^+ \cdot H_2O$ where O_2^+ and O_4^+ are the precursor ions. Other hydrates are generated according to

$$H_3O^+ \cdot (H_2O)_n + H_2O + M \rightarrow H_3O^+ \cdot (H_2O)_{n+1} + M \qquad (42)$$

All these new clusters recombine with the free electrons through the dissociative recombination process to produce neutral products.

A schematic diagram shown in Fig. 2 illustrates the flow of the positive charge in a disturbed wet air. This diagram clearly shows more complication compared to dry air scheme presented in Figure 1.

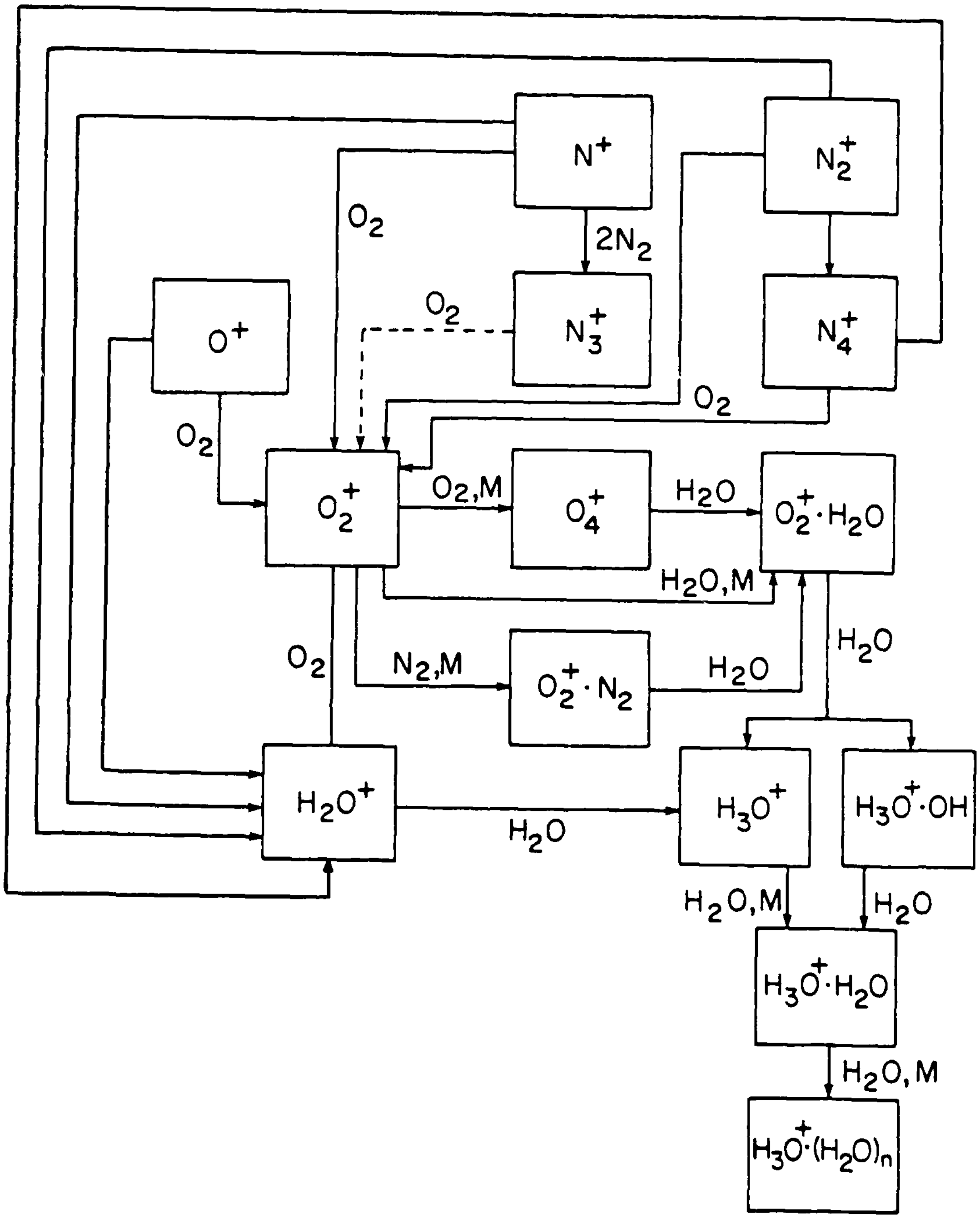

Fig. 2 — Disturbed wet air positive ion flow charts

IV. REACTION RATES

The relevant reaction rates pertinent to the early time wet air chemistry code is given as a function of temperature, if the temperature dependence is known; otherwise the room temperature values are presented. A review of these and other rates is to be reported elsewhere[7].

Table 1. LIST OF REACTIONS AND THEIR COEFFICIENTS

Reaction	Rate Coefficient	Reference
$N_2^+ + e \rightarrow N + N$	$4.3 \times 10^{-8}\ (T_e)^{-0.39}$	8
$O_2^+ + e \rightarrow O + O$	$1.5 \times 10^{-8}\ (T_e)^{-0.7}$, $T_e \leq 0.1$	8
	$2.1 \times 10^{-8}\ (T_e)^{-0.5}$, $T_e > 0.1$	8
$N_4^+ + e \rightarrow N_2 + N_2$	$3.4 \times 10^{-8}\ (T_e)^{-1.1}$	9, 10
$N_3^+ + e \rightarrow N + N_2$	$1.75 \times 10^{-8}(T_e)^{-1.0}$	6,10
$O_4^+ + e \rightarrow O_2 + O_2$	$3.4 \times 10^{-8}\ (T_e)^{-1.0}$	6,10
$H_3O^+ + e \rightarrow H + H_2O$	$3.2 \times 10^{-7}\ (T_e)^{-1.0}$, $T_e \leq 0.86$	6,10
	$2.5 \times 10^{-8}\ (T_e)^{-1.2}$, $0.26 \leq T_e \leq 2.15$	11
	$3.05 \times 10^{-8}(T_e)^{-1.43}$ $2.15 \leq T_e \leq 8.6$	11
$H_2O^+ + e \rightarrow OH + H$	$2.7 \times 10^{-8}\ (T_e)^{-0.5}$	Estimated
$H_3O^+ \cdot H_2O + e \rightarrow$ $2H_2O + H$	$1.6 \times 10^{-6}\ (T_e)^{-0.15}$	6,10
$H_3O^+ \cdot (H_2O)_2 + e \rightarrow$ $3H_2O + H$	$4.2 \times 10^{-6}\ (T_e)^{-0.05}$	6,10

Table 1. (continued)

$O_2^+ \cdot H_2O + e \rightarrow O_2 + H_2O$	$7.2 \times 10^{-7}\ (T_e)^{-0.2}$		6
$H_3O^+ \cdot OH + e \rightarrow H_2O + H + OH$	$9.6 \times 10^{-7} (T_e)^{-0.2}$		6
$e + M + (A^+, A_2^+) \rightarrow (A, A_2) + M$	$5.9 \times 10^{-31}\ (T_e)^{-2.5}$		6
$e + e + (A^+, A_2^+) \rightarrow e + (A, A_2)$	$4.3 \times 10^{-27}\ (T_e)^{-4.5}$		6
$N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$	$3.1 \times 10^{-35}\ (T_a)^{-3.9}$		12,13
	$1.3 \times 10^{-30}\ (T_a)^{-1.0}$		10
$N^+ + 2N_2 \rightarrow N_3^+ + N_2$	$4.5 \times 10^{-31}\ (T_a)^{-1.0}$		10
$O_2^+ + 2O_2 \rightarrow O_4^+ + O_2$	$1.9 \times 10^{-35}\ (T_a)^{-3.2}$		14
$O_2^+ + M + H_2O \rightarrow O_2^+ \cdot H_2O + M$	$1.75 \times 10^{-31} (T_a)^{-2.0}$	$M=N_2$	10
	$1.43 \times 10^{-31} (T_a)^{-2.0}$	$M=O_2$	10
$H_3O^+ + H_2O + M \rightarrow H_3O^+ \cdot H_2O + M$	$2.1 \times 10^{-30}\ (T_a)^{-2.0}$	$M=N_2$	10
	$1.4 \times 10^{-33}\ (T_a)^{-4.0}$	$M=O_2$	10
$H_3O^+ \cdot H_2O + H_2O + M \rightarrow H_3O^+ \cdot (H_2O)_2 + M$	$1.4 \times 10^{-30}\ (T_a)^{-2.0}$	$M=N_2$	10
	$7.8 \times 10^{-33}\ (T_a)^{-4.0}$	$M=O_2$	10
$N^+ + O_2 \rightarrow O_2^+ + N$	2.8×10^{-10}	$, T_a \leq 0.39$	10,15

Table 1. continued

	$5.3 \times 10^{-10} (T_a)^{0.57}$	$T_a > 0.39$	
$N_2^+ + O_2 \rightarrow O_2^+ + N_2$	$2.7 \times 10^{-12} (T_a)^{-0.8}$	, $T_a \leq 0.3$	15
	$4.2 \times 10^{-11} (T_a)^{1.4}$	, $T_a > 0.3$	15
$N_3^+ + O_2 \rightarrow NO^+ + N_2 + O$	5.1×10^{-11}		16
and $NO_2^+ + N_2$	$8.8 \times 10^{-12} (T_a)^{-0.52}$		17
$N_4^+ + O_2 \rightarrow O_2^+ + 2N_2$	2.5×10^{-10}		16
$O^+ + O_2 \rightarrow O_2^+ + O$	$4.6 \times 10^{-12} (T_a)^{-0.4}$	$T_a \leq .155$	18
	$1.0 \times 10^{-10} (T_a)^{1.0}$	$T_a > .155$	
$N^+ + H_2O \rightarrow H_2O^+ + N$	2.8×10^{-9}		16
$N_4^+ + H_2O \rightarrow H_2O^+ + 2N_2$	3.0×10^{-9}		16
$O^+ + H_2O \rightarrow H_2O^+ + N_2$	3.2×10^{-9}		16
$N_2^+ + H_2O \rightarrow H_2O^+ + N_2$	2.8×10^{-9}		16
and $N_2^+H + OH$	a=0.82 b= .18		
$N_3^+ + H_2O \rightarrow H_2NO^+ + N_2$	3.3×10^{-10}		16
$O^+ + N_2 \rightarrow NO^+ + N$	7.5×10^{-10}	$T_a \leq 0.1$	15,18
	$3.2 \times 10^{-11} (T_a)^{1.38}$	$T_a > 0.1$	
	$T_a = T_v$		
$O_4^+ + H_2O \rightarrow O_2^+ \cdot H_2O$	1.5×10^{-9}		19

Table 1. Continued

$O_2^+ \cdot H_2O + H_2O \rightarrow H_3O^+ \cdot OH + O_2$	1.2×10^{-9}	19
$\rightarrow H_3O^+ + OH + O_2$	a=0.83 b=0.17	
$H_3O^+ \cdot OH + H_2O \rightarrow H_3O^+ \cdot H_2O + OH$	1.4×10^{-9}	19
$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	1.8×10^{-9}	10
$H_2O^+ + O_2 \rightarrow O_2^+ + H_2O$	2.0×10^{-10}	10
$O^+ + O^- \rightarrow O + O$	$4.3 \times 10^{-8}\ [T_a]^{0.5}$	6,10
$N^+ + O^- \rightarrow N + O$	$4.1 \times 10^{-8}\ [T_a]^{0.5}$	6,10
$O_2^+ + O^- \rightarrow O_2 + O$	$1.6 \times 10^{-8}\ [T_a]^{0.5}$	6,10
$O_2^+ + O_2^- \rightarrow O_2 + O_2$	$6.6 \times 10^{-8}\ [T_a]^{0.5}$	6,10
$N_2^+ + O_2^- \rightarrow N_2 + O_2$	$2.5 \times 10^{-8}\ [T_a]^{0.5}$	6,10
$X^+ + Y^- \rightarrow X + Y$	$1.6 \times 10^{-8}\ [T_a]^{0.5}$	20
$A^+ + B^- + M \rightarrow A + B + M$	$2.9 \times 10^{-29} [T_a]^{2.5}$	6
$X^+ + Y^- + M \rightarrow X + Y + M$	$1.0 \times 10^{-29} [T_a]^{2.5}$	6
$e + O_2 + O_2 \rightarrow O_2^- + O_2$	$3.6 \times 10^{-31} (\frac{1}{T_e})\ \mathrm{Exp}(-\frac{0.052}{T_e})$	21
$e + O_2 + N_2 \rightarrow O_2^- + N_2$	1.0×10^{-31}	21
$e + O_2 + H_2O \rightarrow O_2^- + H_2O$	1.4×10^{-29}	21

Table 1. Continued

$e + O_2 \rightarrow O^- + O$	$1.5x10^{-10}(T_e)^{-1.0}$ Exp $(-5/T_e)$	22

T_e and T_a are in eV

V. SPECIES AND TEMPERATURES

The early time disturbed wet air chemistry code solves a set of rate equations to calculate the time histories of: N^+, N_3^+, N_4^+, O^+, O_2^+, O_4^+, H_2O^+, H_3O^+, $H_3O^+ \cdot OH$, $O_2^+ \cdot H_2O$, $H_3O^+ \cdot H_2O$, O_2^- and $\bar{O}$. On the other hand, the electron density is calculated via the charge neutrality condition. In addition to the above species, the electron temperature, T_e, the N_2 vibrational temperature, T_v, and the neutral species temperature, T_a, are calculated. The set of the rate equation for species and temperatures are solved by a computer program devised by D. Strickland of Beers Associates.

The calculation of T_e, T_v, and T_a are necessary because (see Table 1, Section 4) various relevant deionization reactions are temperature dependent.

The calculations of these temperatures requires data on all appropriate cross sections[23] for elastic and inelastic processes in order to account for the energy loss by electrons in air. These cross sections are then utilized along with the electron velocity distribution to obtain the relevant rate coefficients. The current rate coefficients used in this code are based on a previous set of cross sections[24], some of which have been modified[25] to the most current data. The calculation of the vibrational temperature and the energy stored in the N_2 vibrational mode follows a method reported previously.[26] The neutral temperature, on the other hand, is calculated ab initio, where the heating sources are the elastic electron neutral, electron ion collisions, dissociative recombination, charge exchange and the arrangement processes.

The ohmic heating of the thermal electrons is considered in the code by solving a simple circuit equation.[27] This circuit equation relates the net current I_n, to the induced electric field, E_z, via,

$$L \frac{dI_n}{dt} = E_z$$

Where L is the inductance per unit length and is defined as

$$L = \frac{2}{C^2} \left[\log \left(\frac{R}{r_b} \right)^2 + \frac{1}{4} \right]$$

Where r_b is the beam current radius and $R > r_b$ is the radius where conductivity in the plasma sheath falls to $\frac{C}{4\pi R}$. The net current, on the other hand, is

$$I_n = I_b + n r_b^2 \sigma E_z$$

σ is the conductivity and I_b is the beam current.

The conductivity σ is defined as

$$\sigma = \frac{e^2}{m} \frac{Ne}{\nu_m}$$

Where ν_m is the electron momentum transfer collision frequency and is the sum of the electron neutral and electron ion collision frequencies.

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